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RAPID METHOD FOR DETERMINING NO_x EMISSIONS IN FLUE GASES

by

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This report discusses the NO_x compliance procedure (Method 7) for stationary sources and the attempts to improve the procedure and decrease analytical time. When the procedure is rigorously followed, Method 7 was found to be precise and to give reproducible results. To decrease the time necessary to oxidize NO to NO_2, Method 7 was modified by adding an ozone lamp. Good agreement (±12% or less) was found between nitrate measurements using Method 7 and measurements using modified Method 7. Future work incorporating an ozone lamp into an integrated sampling apparatus is discussed.

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SECTION I
INTRODUCTION

Wet chemical methods for the determination of nitrogen oxides (NO_x) in gaseous mixtures are generally variations of either the phenoldisulfonic acid[1] procedure or the Saltzman[2] procedure.

The phenoldisulfonic acid (PDS) method, although not as sensitive as the Saltzman procedure, is sufficiently accurate for determining NO_x levels emitted by combustion sources and nitric acid manufacturing plants (50 to 2000 ppm). In 1971, the Environmental Protection Agency therefore, promulgated the PDS method (called EPA Method 7) as the compliance test analytical technique to be used in determining NO_x emissions levels from fossil-fuel-fired steam generators and from nitric acid plants.[3]

Various workers, including Chamot et al. in their original publication,[1] have addressed the sources of error and shortcomings of the PDS method. Beatty,[4] for example, addressed problems of sample bottle contaminations, preparation of the PDS reagent, instability of the absorbing solution (hydrogen peroxide and sulfuric acid) as a function of time, and requirements for spectrophotometric readings. He concluded that the chief sources of error in the analytical method were improper preparation of the PDS reagent, long-term stability of the hydrogen peroxide absorbing solution, and the general use of inferior grade chemicals in the preparation of reagents - all of which result in variable "blank" readings and high sample standard deviations.

Di Martini,[5] utilizing the fast oxidation of nitric oxide by ozone, developed a semi-continuous analyzer for NO measurements in the 0-10 ppm range. Using the more rapid gas-phase reaction $NO + O_3 \rightarrow NO_2 + O_2$ rather than the $2NO + O_2 \rightarrow 2NO_2$ reaction as in the PDS method, and then reading the nitrate ion concentration via a specific ion electrode (SIE) technique, he was able to reduce analysis time to one hour. Although he did not attempt analysis at higher concentrations, there is no apparent reason why the technique would not be applied to emissions from fossil-fuel-fired steam generators. Driscoll et al.[6], using molecular oxygen as the NO oxidizing agent and the nitrate SIE technique for determining species concentration, obtained results similar to those of Di Martini.

Driscoll also applied the technique to the analysis of NO_x emissions in both oil- and gas-fired combustion effluents with satisfactory results when compared with the PDS method.

Both Singh et al.[7] and Harman and Neti[8] utilized the fast oxidation reaction between NO and O_3 in designing instruments for the continuous analysis of NO in exhaust gases. The Singh method is based on the rapid conversion of NO to NO_2 through ozonation and the subsequent determination of the NO concentration using a continuously flowing optical photometer. The problems encountered in this system included a less than 1:1 conversion efficiency of NO to NO_2 for a constant ozone concentration with variable nitric oxide concentration and a lack of sensitivity to flow parameter fluctuations by the detector. The Harman and Neit instrument effects conversion of NO to NO_2 in a similar manner to the Singh instrument and determines NO_2 via a continuous Saltzman method. Prior to the determination of NO_x by the Saltzman technique, these workers incorporated an argentic oxide scrubber to remove excess ozone and other possible interferants.

The PDS method has three disadvantages: (1) an exceptionally long oxidation time is required for analysis, (2) a laborious (2-4 hours) evaporation step is needed and (3) the fact that the samples are taken in an evacuated flask for a 15- to 20- second time interval can require numerous determinations to account for possible source fluctuations.

Margolis and Driscoll[9] addressed the reaction kinetics problem and concluded that oxidation of NO to the water soluble nitrate species using molecular ozygen suffered from several problems. For moderate source level concentrations (400-500 ppm), the calculated oxidation time for 97 percent of the NO was about 28 hours. Because the reaction time was dependent on (P_{no}),^{2} for lower NO concentrations (below 100 ppm), calculations showed that oxidation would require as long at 50 hours to achieve 97 percent completion. They concluded that by increasing P_{o2} or by using an oxidant that is more reactive than molecular oxygen, the analysis time could be significantly reduced. The former principle has been used by DuPont in its Model 460 NO_x analyzer. With this device, the NO is converted to NO_x by oxygen at high pressures, and the oxidation time is reduce to about 10 minutes.

Coulehan and Lang[10] modified the PDS procedure in an effort to reduce analysis time. Their technique invclves minimizing sample volume and absorbing solution volume and performing the PDS nitration step in 50 percent H_2SO_4 rather than fuming H_2SO_4 as called for in Method 7. The analysis time was substantially reduced, and excellent agreement between the original and modified procedures was obtained.

This report discusses attempts to reduce the time of analysis for the EPA Method 7 (POS) procedure, modifications to the procedure, and the need for future work based on the results reported here.

SECTION II
CONCLUSIONS

Based on initial experiments reported here, the following conclusions may be made:

1. Method 7 appears to be a precise and repeatable laboratory procedure when the written directions are carefully and scrupulously followed. Typical standard deviations of ±5 percent of the mean value are attainable when analyzing cylinders of NO in N_2. Predictions of precision in actual field applications are more problematic, however, because of existing spatial and temporal macro and micro fluctuations in sources.
2. The precision of both Method 7 and the Modified Method 7 described here is operator dependent. After suitable training and practice, experienced personnel should be able to achieve 95 to 97 percent reproducibility on successive determinations from the same NO cylinder of source.
3. The use of ozone generation is a practical technique for obviating the necessity for a lengthy oxidation step for converting NO to determinable nitrate. In general, agreement between Method 7 and Modified Method 7 analyses for a cylinder of NO in N_2 was within ±12 percent at the least, and better in most cases.
4. Observations that additional O_2 affected the procedure are unresolved at this time. One operator concluded that it was necessary to add O_2 to the sampling flask to achieve reaction completion with a reasonable time (30 minutes or less). In another case, a different operator concluded that O_2 addition was detrimental to the completion of the $NO+O_3 \rightarrow NO_2$ reaction. Calculations of O_2 additions necessary to generate sufficient O_3 to convert stack level NO concentrations (200-600 ppm) show that O_2 concentrations in the excess air of the combustion process are more than ample. Typically, there is 4-6 percent excess air or about 1-1.5 percent O_2 available. The disagreement between the operators appears to reflect variations in the procedure used and should be resolved by adhering strictly to the specific procedure.

5. The absolute accuracy of Method 7 appears to be in question. In analyzing four NO-in-N_2 cylinders purchased from various suppliers, labelled cylinder concentrations were 10-20 percent higher than determined either by Method 7 or the modified method. In the case of low-concentration cylinders (below 100 ppm), analyses were as much as 50 percent low.

SECTION III
RECOMMENDATIONS

1. The accuracy of Method 7 should be established, especially with respect to relatively low concentration cylinders and to cylinder concentrations at or near the emission standard for the particular source. This is important because of the pending promulgation of performance specifications for SO_2 and NO_x continuous monitors. These specifications require instrumental calibration against cylinders that have been standardized using the respective reference methods.
2. A substitute for the grab sampling technique for NO_x used in EPA Method 7 should be developed to reduce the large number of samples needed to achieve an acceptable mean value and confidence interval in the present technique. Development of an integrated sampling technique that uses the Modified Mehtod 7 procedure is presently being investigated by EPA. The technique employs a 6-liter sampling flask with connections for a thermometer, a pressure gauge, an ultraviolet irradiation lamp, a sampling line, an absorbing solution drain outlet, and a vacuum pump. A critical orifice is interfaced through the sampling line to vary the sampling period from 2 to 30 minutes. Although initial studies with the system have been limited to analyzing NO-in-N_2 cylinders, the results have been encouraging. After further laboratory studies, the system will be tested at a coal-fired power plant and a nitric acid plant.

SECTION IV
EXPERIMENTAL DESIGN AND PROCEDURE

METHOD 7

In the Method 7 procedure, a grab sample is collected in a 2-liter flask evacuated a 75-mm pressure and containing a weak sulfuric acid-hydrogen peroxide solution. The principal species present in the sample is NO. Because of its low solubility in water, the NO is converted to the more soluble nitric acid via the following reactions:

$$NO + NO_2 \xrightarrow[\text{(slow)}]{O_2} N_2O_3 \text{ or } N_2O_5 \xrightarrow[H_2O_2]{\text{aqueous acidic}} HNO_3 \text{ (analyzed for nitrate)}$$

Oxidation is effected by allowing the sample to stand overnight in the sampling flask. After removal of the absorbing solution containing the nitrate sample, the solution is neutralized to fix the nitrate as the ammonium salt. This step is followed by evaporation to dryness on a steam bath and reaction with the 1-phenol-2,4, disulfonic acid to effect nitration of the benzene ring. The resulting yellow solution produced by neutralization of the nitrate-PDS solution is determined by spectrophotometric analysis at 410 nanometers (nm). A calibration curve (Figure 1) is prepared using potassium nitrate as a primary standard and plotting NO_2 in micrograms (µg) versus the spectrophotometrically determined absorbance. The slope of the absorbance versus the µg NO_2 straight line has been found to be 0.0015 using a B&L Spectronic 20 instrument at 410 nm. The most suitable concentration range for the analysis is 0 to 400 µg NO_2. More highly concentrated solutions are diluted to bring them within the known linear portion of the plot.

MODIFIED METHOD 7

The modified procedure deviates from the promulgated Method 7 procedures as follows:

1. Method 7 employs a 2-liter, round bottom flask protected against implosion or breakage as shown in Figure 2. Modified

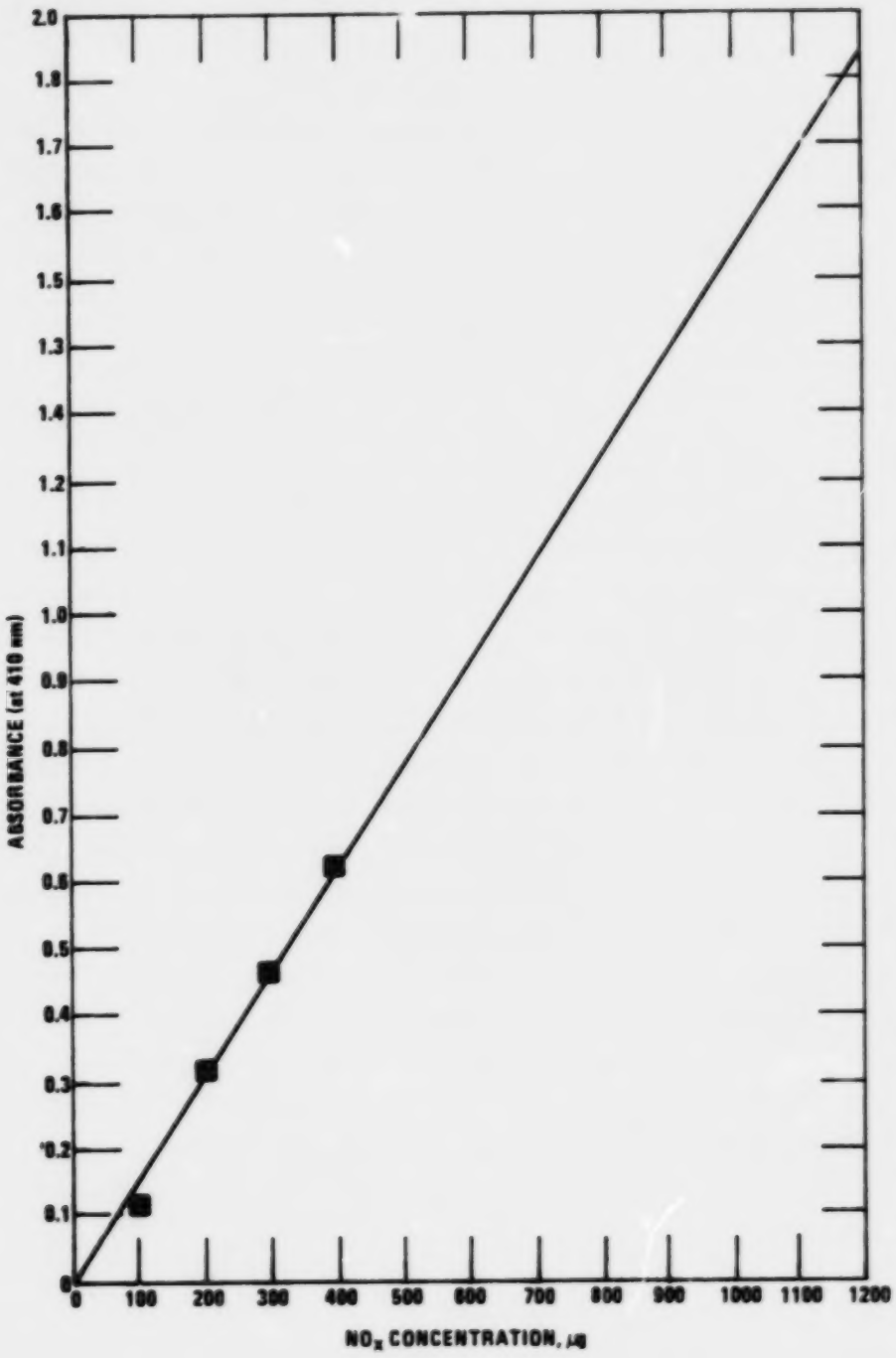

Figure 1. Method 7 calibration curve.

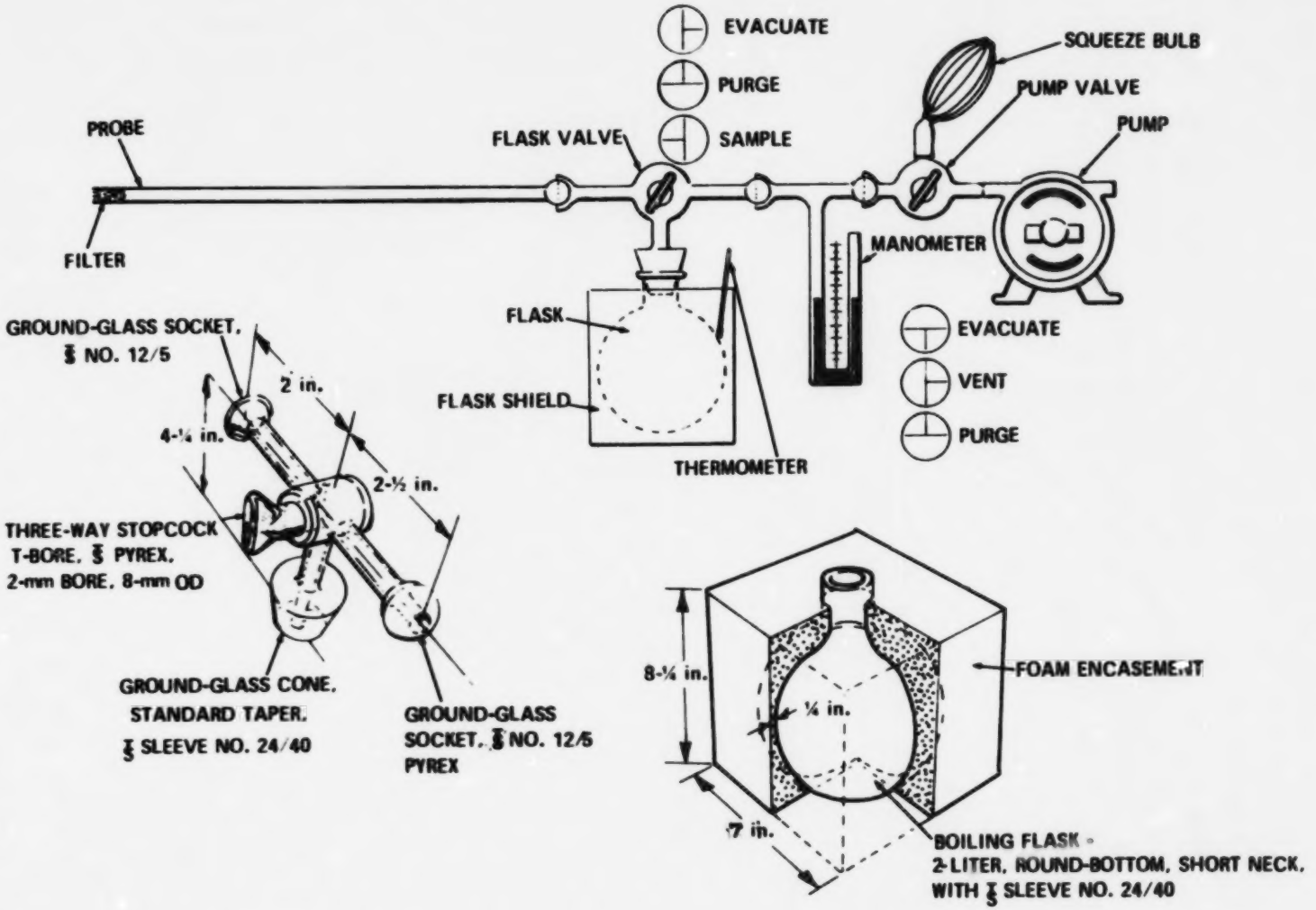

Figure 2. Sampling train, flask valve, and flask.

Method 7 requires a 2-liter flask protected against implosion or breakage. The sampling flask for Modified Method 7 is shown in Figure 3.

2. Method 7 calls for a 5-minute shaking time after taking the sample and then allowing the flask to sit for a minimum of 16 hours. In the Modified Method 7, the sample is magnetically stirred and simultaneously irradiated using an ultraviolet lamp.

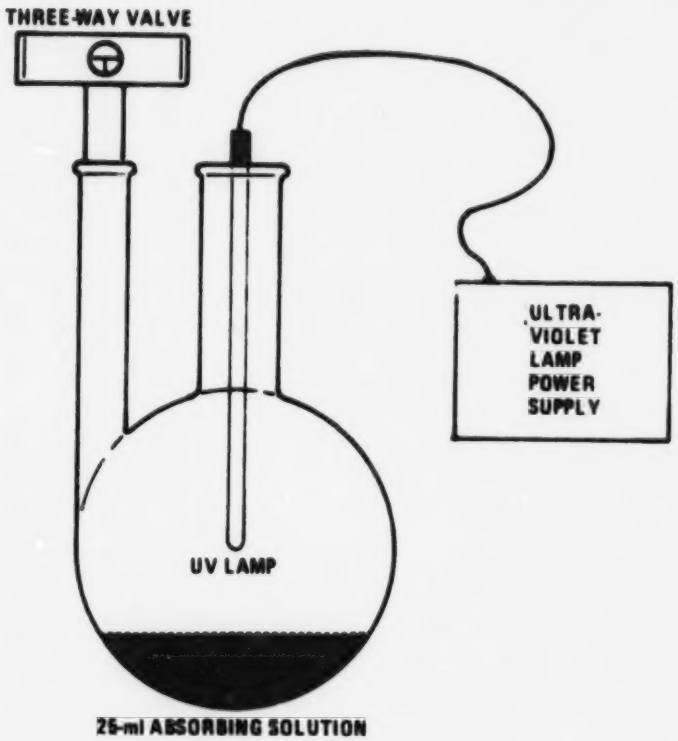

Figure 3. Ultraviolet 2-liter sampling flask.

SECTION V
EXPERIMENTAL RESULTS

LABORATORY STUDIES

After observing variability in Method 7 and Modified Method 7 analytical values, efforts were made to improve accuracy and assess repeatability over a range of NO_x concentrations. The effect of various procedural inconsistancies was investigated, and the subsequent application of any procedural amendment was evaluated. The utilization of a precise analytical procedure for both Method 7 and for the more rapid Modified Method 7 is critical.

Sample Line Purging with Sample Gas

Long sampling line configurations have been found to affect accuracy and repeatability of the NO_x analysis using either method. This effect can be understood in terms of the "dead space" or volume of the sample lines in relation to the volume of the flask (approximately 2 liters). The longer the sample lines, the more marked the effect on the measurement accuracy. The results, in fact, can be as much as 10-15 percent low. For this reason, live purging with the sample gas whether it be from a cylinder or a stack must be done before the sample gas is drawn into the flask.

The data in Table 1 reflect the errors resulting from incomplete sample line purging in laboratory studies in which a 2-liter flask was utilized. The magnitude of the error depended on flask volume, sample line volume, and source pressure relative to atmospheric. Although the sample lines were evacuated to 3 inches of mercury (absolute) as was the sampling flask. Depending on conditions and equipment, field errors could be equal to or greater than those mentioned in this report. The procedures followed here were identical to those in the Federal Register[3] except as noted in the table. A complete data summary of the laboratory studies in tabular form may be found at the end of this section.

Table 1. EFFECT OF PURGING SAMPLES

Labeled cylinder concentration, ppm NO_x	Purged line, ppm NO_x	Standard deviation, ppm NO_x	Number of samples	Unpurged line, ppm NO_x	Standard deviation ppm NO_x	Number of samples
510	428	5	6	356	13	4
60	23	3	4	28	3	6

The 16.9 percent error caused by unpurged sample lines in Method 7 for the 510 ppm cylinder gas is illustrated in Figure 4. Method 7 data accumulated from the 60-ppm gas cylinder indicated a slight increase in reported NO_x; this increase may not be significant due to the standard deviations of the various measurements.

Random Variability Resulting from Human Error

After refining the analytical procedure to some degree, the fluctuations observed in reported NO_x caused by equipment variability (flask volume), incomplete transfers of absorbing solutions during analysis, and other factors of nominal concern were tested for their contributions to the standard deviation. To observe such effects, it was necessary to eliminate fluctuations in sampling and analytical procedures. To ensure that the samples were drawn as representatively as possible, a manifold was designed to evacuate and monitor pressure as well as to allocate sample gas equally to all samples (Figure 5). In addition, samples drawn through the manifold were analyzed concurrently to minimize error.

The data presented in Table 2 reflect any variation resulting from human error, random equipment failure, or both.

Table 2. MANIFOLD STUDY OF RANDOM VARIABILITY

Labeled cylinder concentration, ppm NO_x	Actual concentration, ppm NO_x	Procedure[a]	Average concentration, ppm NO_x	Standard deviation ppm, NO_x	Percent standard deviation[b]	Sample Number
510	428	M7	427.9	5.36	1.2	1-3
500	455	M7	456.96	4.20	0.9	4-6
500	455	M7	466.53	15.03	3.2	7-9
500	455	MM7	387.5	29.1	8.8	17-18
500	455	MM7	357.05	31.45	7.5	14-15
575	untyped	MM7	466.2	8.2	1.7	1-2
575	untyped	MM7	481.6	12.5	2.6	3-4

[a] M7 = Method 7; MM7 = Modified Method 7.

[b] Cumulative average of percent standard deviation = 3.7 percent of reported NO_x values (all cylinder concentrations).

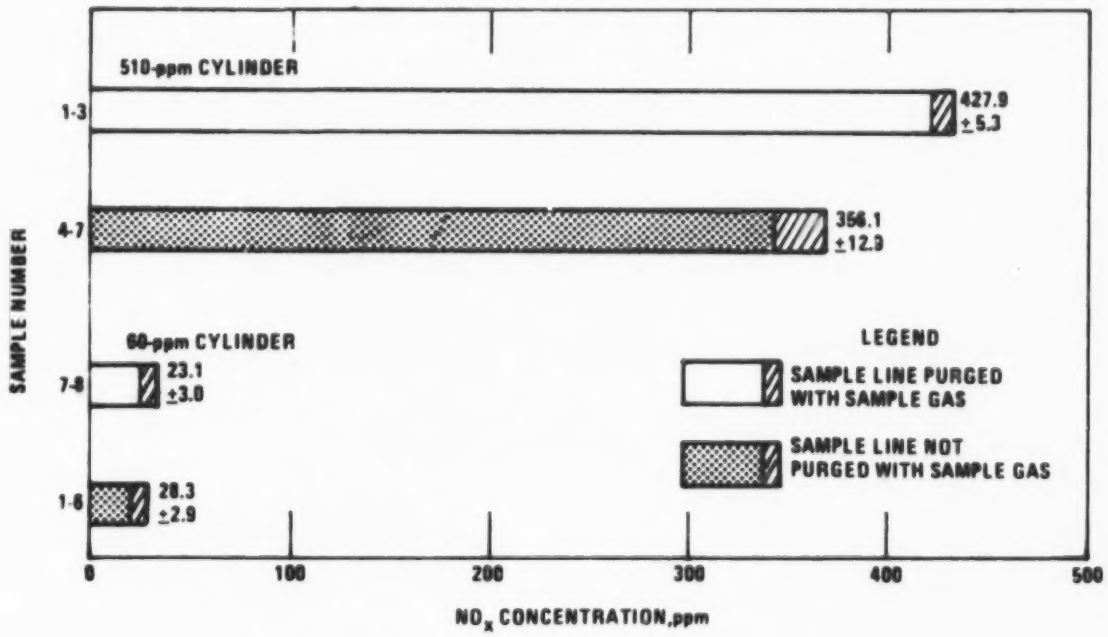

Figure 4. Effect of sample-line purging on sample recovery in the M7 standard procedure.

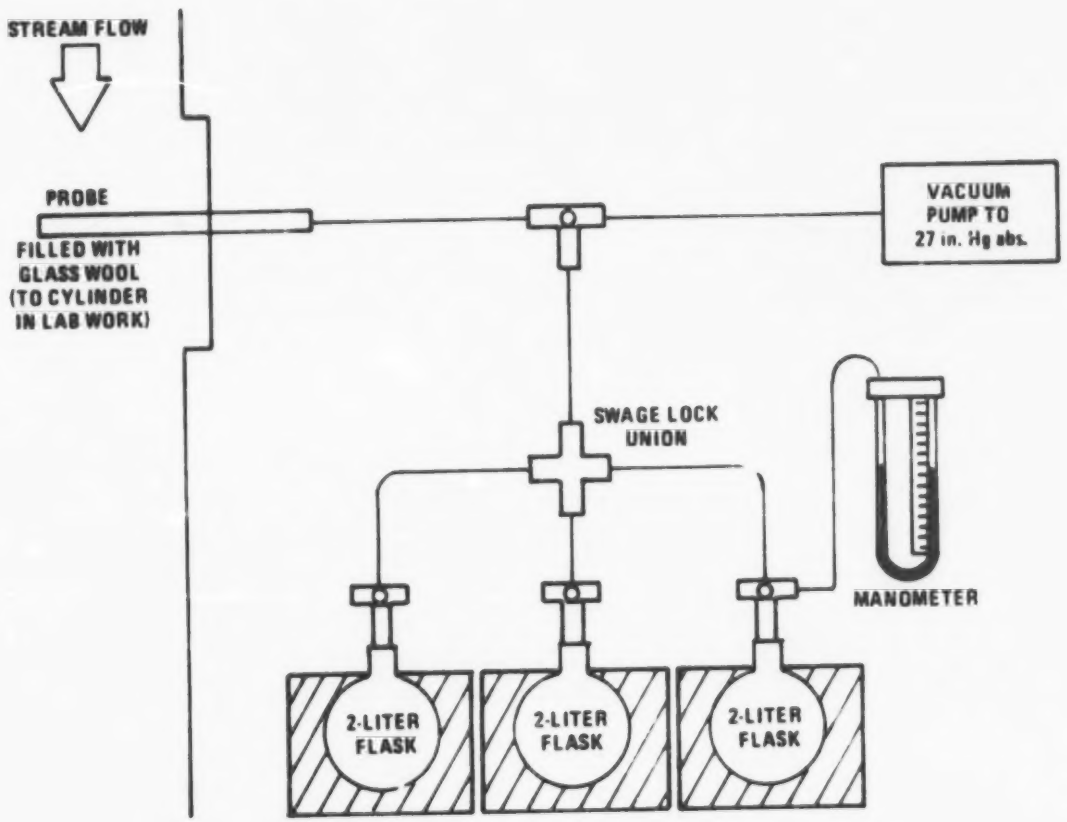

Figure 5. Sampling manifold diagram.

From these data, one may assume that, with all conditions held constant within experimental groups, a standard deviation of ~3.7 percent is attainable. Any standard deviation significantly greater than 3.7 percent is considered to be the result of experimental design problems or equipment failure.

Irradiation Study of Modified Method 7

The $2NO+O_2 \rightarrow 2NO_2$ reaction in the recovery step of Method 7 is slow and determines the rate at which the sample is evaluated. Reduction of the 16-hour waiting period to approximately 15 minutes can be effected, however, by expediting the oxidation of NO to NO_2. Rapid generation of ozone, which rapidly oxidizes nitric oxide,[5,7] is accomplished in the Modified Method 7 procedure by using an in-flask ultraviolet photochemical lamp.

The time of ultraviolet irradiation in Modified Method 7 seems critical to its repeatability. Because the duration of ultraviolet irradiation determines the relative concentration of O_3 generated within a sample flask, the consistent application of ultraviolet irradiation among flasks is necessary to ensure that equivalent concentrations of O_3 are available for oxidation. In an EPA laboratory study, the ultraviolet irradiation period necessary to effect a 90 percent conversion (based on Method 7 data) was reported to be 15 minutes (See Table 3). During extensive testing of Modified Method 7 in January 1975, some variability observed in the NO_x response level was attributed to the inconsistent irradiation periods administered in previous tests.

Table 3. IRRADIATION OF GAS PHASE FOR MODIFIED METHOD 7

Evaluation criteria[a]	Labeled cylinder concentration, ppm[b]	O_2 added[c]	Reported concentration, ppm	Flask volume, ml.	µg NO_x	Initial pressure, in. Hg	Final pressure, in. Hg
0 uv							
5 sitr	560	yes	107	2080	300	3.0	29.4
10 stir	560	yes	25	2120	72	2.0	29.4
30 stir	560	yes	42	2078	120	2.2	28.6
15 stir	560	no	67	2078	185	3.0	29.6
			Average ppm = 60.2 ± 26.8 for O_2				
5 uv							
5 stir	560	yes	456	2025	1220	2.4	31.2
5 stir	560	yes	457	2062	1290	2.3	28.6
			Average ppm = 456.5 ± 0.5 for O_2				
10 uv							
10 stir	560	yes	502	2025	1270	2.2	31.7
10 stir	560	yes	523	2062	1404	2.1	30.4
			Average ppm = 512.5 ± 10.5 for O_2				
15 uv							
15 stir	560	yes	622	2025	1700	2.1	29.3
15 stir	560	no	129	2066	357	3.0	29.4
15 stir	560	no	134	2062	375	3.0	29.4
15 stir	280	yes	245	2025	648	2.3	29.6
15 stir	280[d]	yes	283	2062[d]	444	2.2	17.5
			Average ppm = 622.0 for O_2				
30 uv							
30 stir	280	yes	258	2062	690	2.2	29.5
30 stir	280	yes	267	2025	712	2.2	29.7
30 stir	560	no	183	2078	540	2.0	28.5
30 stir	560	no	146	2025	400	2.2	29.3
30 stir	560	no	174	2062	500	2.1	28.5
30 stir	560	yes	578	2062	1650	2.0	28.6
			Average ppm = 578 for O_2				

[a] Indicates time (in minutes) of irradiation using the photochemical lamp and the time (in minutes) of stirring the absorbing solution.

[b] The manufacturer's values as determined by a chemiluminescence analyzer.

[c] Indicates whether cylinder oxygen was added to flask before sampling.

[d] Flask half filled.

The high standard deviation observed in early Modified Method 7 tests is believed to be caused by the O_3 concentration differential between flasks and/or the heat output of the operating ultraviolet lamp that would allow a faster and more complete reaction for those samples that were irradiated longer.

In attempts to increase the recovery of NO_x through the adoption of Modified Method 7, longer ultraviolet irradiation periods were evaluated. A comparison of samples drawn from a 500 ppm cylinder (actually 455 ppm) utilizing the manifold is shown in Table 4. The net gain in recovery of NO_x through increasing the ultraviolet irradiation period from 15 to 30 minutes was 3 to 10 percent.

The increase in sample recovery discovered during 30 minutes of irradiation would warrant the use of the longer period for future Modified Method 7 work.

Table 4. EFFECTS OF ULTRAVIOLET IRRADIATION TIME

Irradiation time, minutes	Labeled cylinder concentration, ppm NO	Concentrations recovered, ppm NO_x	Standard deviation, ppm
15	500	357.2	±33.01
30	500	398.9	±27.06
			% recovery increase=10.5
15	575	466.2	± 8.2
30	575	481.6	±12.5
			% recovery increase=3.2

Oxygen Study

The effect of adding pure oxygen (O_2) to the Modified Method 7 sampling flask before sampling was investigated. Method 7 samples were not tested for any effect with added oxygen because there is sufficient O_2 present at the 3 in. Hg pressure used in sampling.

Four Modified Method 7 samples were taken--both with and without O_2 addition--to determine whether the percentage of NO_x recovery would increase with extra O_2 available. The samples with added O_2 were taken in the following manner:

(1) the absorbing solution was added to the 2-liter flask, (2) the flask was evacuated to +75 mm Hg pressure, (3) cylinder O_2 was then introduced to the flask until atmospheric pressure was attained, (4) the flask was reevacuated to +75 mm Hg pressure and was then ready for use.

The data presented in Table 5 indicate that at higher NO_x concentrations (around 500 ppm) the addition of O_2 to the Modified Method 7 sample flasks had an adverse effect on the NO_x recovery as compared with those samples without O_2. This result is difficult to explain because there is a conflict in various sets of data (See Tables 3 and 5). Nevertheless, in tests using a cylinder with a labeled concentration of 510 ppm NO in N_2, the data indicate a net decrease of recovered NO_x when the flask is purged with O_2 prior to evacuation for sampling. Three samples drawn with no O_2 addition averaged 372.7±20.3 ppm (Table 5). Four flasks purged with O_2 prior to the sampling evacuation averaged 250.9±23.2 ppm. The effect of O_2 was significant, and the net result was a decrease in recovery of 121.8±23.2 ppm NO_x. The observed difference was puzzling because previous experience with O_2 in Modified Method 7 suggested that any effect should have been either nominal or favor a more complete recovery of NO_x. An identical procedure was utilized for a cylinder containing 575 ppm NO in N_2. Unlike the samples from the 510 ppm cylinder, however, the ultraviolet period was set for exactly fifteen minutes, utilizing a sampling manifold, two samples were simultaneously drawn and purged with O_2 to assure that variables would be minimized. The NO_x level was calculated to be 466.2±8.2 ppm. The control group--one with no O_2 purging--was sampled exactly as those to which O_2 had been added. The reported NO_x value for no O_2 addition was 481.6±12.5 ppm NO_x. Here again, a reduction in NO_x recovery was noted when the O_2 was added. Although the diminution was not as pronounced in this study as it was in the 510 ppm study, the net recovery of NO_x through O_2 addition was decreased by 15.4±12.5 ppm.

A study of the effect of O_2 addition on low NO_x concentration sources was investigated on a cylinder labeled 60 ppm (actual concentrations by Method 7 was 28.3 ppm). At this low concentration, the expectation that observable trends would be difficult to detect was confirmed (See

Table 5. OXYGEN EFFECTS AT VARIOUS CONCENTRATIONS

Labeled cylinder concentration, ppm	Variable	NO_x concentration, ppm
510	O_2 addition	250.9±23.2
510	No addition	372.7±20.3
575	O_2 addition	466.2±8.2
575	No addition	481.6±12.5
60	O_2 addition	31.9±3.8
60	No addition	28.7±3.3

Table 5). The Modified Method 7 flask samples that had no O_2 addition averaged 28.7±3.3 ppm NO_x over three trials; whereas, the O_2-treated samples registered 31.9±3.8 ppm NO_x over four samples. At this low concentration, the inverse relationship previously reported between O_2 and recovered NO_x was not observed if one considers the standard deviation range.

Method 7 Evaluation and Cylinder Typing

In order to evaluate the Modified Method, Method 7 samples were taken at various cylinder concentrations and were subsequently used for comparison with Modified Method 7 data.

The Method 7 procedure included: purging the sample line with the sample gas prior to final evacuation, pipetting the 25 milliliters of absorbing solution into the flask, agitating the solution via magnetic stirrer to maximize gas-liquid contact, and waiting the required 16 hours after sampling. The sample was analyzed as prescribed in the Federal Register.[3] The data in Table 6 relates the NO concentrations to the nominal cylinder values.

Table 6 METHOD 7 NO_x CYLINDER CALIBRATION

Labeled cylinder concentration, ppm	Method 7 average, ppm	Standard deviation, ppm	Number of samples in calculation
510[a]	427.9	5.36	3
500	454.9	10.48	9
60	28.3	2.9	6

[a]Old, low-pressure cylinder that may have degenerated over time was used.

The magnitude of standard deviations in all cases is consistently low. In percent, ages the standard deviations for the 510, 500, and 60 ppm cylinders are 1.25, 2.30, and 10.25 percent, respectively.

Data accumulated on the "500 ppm" cylinder should be considered most significant because the largest number of samples were drawn from it.

Based on the low standard deviations listed in Table 6 and the repeatability observed over the sampling period, Method 7 may be considered a repeatable and dependable means of determining NO_x when precautions are taken to avoid obvious sources of error (spillage, leakage into evacuated flask, faulty sampling lines, etc.) and when experimental procedure is followed rigorously.

Evaluation of Modified Method 7 Compared with Method 7

The possible utility of Modified Method 7 as a rapid analysis technique was determined by comparing Modified Method 7 values for NO_x with those values determined by Method 7 (reported in the previous section and in the field section).

The accuracy of values reported depends upon the consistency of technique utilized and the ability of the experimenter to minimize human error. Unfortunately, many of the samples analyzed by Modified Method 7 were inadvertently subject to inconsistencies from several sources including human error and leaking equipment. The greatest source of error, however, was undoubtedly the ultraviolet irradiation period because, until the final stages of experimentation, an irradiation period of 15 minutes or lower was assumed to ensure a consistent degree of NO-NO_2 conversion. During subsequent investigation of the effect of the longer irradiation periods, a 15-minute irradiation of samples drawn from the 500 ppm cylinder (454.9 ppm based on Method 7 evaluation) effected a 78.4 percent NO_x recovery (compared with Method 7 data). The 30-minute irradiation period produced a 10.5 percent greater recovery of NO_x than the 15-minute period (41.7 ppm increase). Total recovery of NO_x using the longer irradiation period was 87.7 percent of the Method 7 calibration of the 500 ppm cylinder (454.9 ppm). It may be assumed that the high standard deviations observed in Modified Method 7 (relative to those of Method 7 were partially caused by inconsistent application of ultraviolet irradiation.

Regardless of any potential error or design malfunction, the Modified Method 7 samples compare favorably with their Method 7 counterparts. Modified Method 7 samples from the 510 ppm cylinder averaged 372.7±20.3 ppm NO_x; those obtained by Method 7 averaged 427.9±5.36 ppm. The

correlation between the two methods was 87.1 percent for that cylinder. The correlation between samples from the 500 ppm cylinder tested by the two methods was 87.7 percent.

A peculiar phenomenon was observed in Modified Method 7 data for the low concentration cylinder (60 ppm). Values obtained through use of Modified Method 7 averaged 31.9±3.8 ppm NO_x over four samples; whereas, the Method 7 average, which generally is higher than Modified Method 7 data, was 28.3±2.9 ppm NO_x over six samples. The greater recovery by Modified Method 7 is not deemed significant, however. The equivalent recovery reported by Modified Method 7 at this concentration may reflect stoichiometric considerations involved with O_3 generation and the resultant higher temperatures found in the Modified Method 7 flasks. Nitrogen oxides recovery for the 60 ppm cylinder using the modified method was 12.7 percent higher than that of Method 7.

The laboratory test data are summarized in Figure 6 and Table 7.

FIELD STUDIES

Field studies of Method 7 and Modified Method 7 were undertaken at three stationary sources of nitrogen oxides emissions to determine the relative efficiency of each method. In-stack, continuous source level monitors were employed to establish baseline data at two of the three sampling sites. Initial evaluation was begun at Carolina Power and Light Company's Moncure, N. C., facility; a subsequent assessment was completed at Duke Power Company's Mt. Holly, N. C., facility. Both sources are coal-fired steam generating stations. EPA's Stationary Source Simulator Facility served as the third site.

Stationary Source Simulator Facility Tests

Simulated stack conditions were achieved at the Stationary Source Simulator Facility (SSSF) at the Environmental Research Center, Research Triangle Park, N. C. Nitrogen oxides levels were monitored concurrently by two in-stack instruments and Method 7.

A TECO chemiluminescence NO_x analyzer was utilized as the primary continuous monitoring standard; the use of the Philco-Ford Gas Correlation instrument was limited to monitoring NO levels in the simulator. The TECO instrument, which had been spanned for NO_x by a previously calibrated

TABLE 7. LABORATORY TEST DATA SUMMARY

Test Method and Sample Number	Volume Flask	Remarks	NO_x, ppm	TECO, ppm	Absorbance	NO_2, mg	Pressure, in.Hg		Temperature, °R	
							Final	Initial	Final	Initial
Modified Method 7 575 cylinder (-ppm)										
1	2123	Gas-purged line; with O_2; manifold; 15 min uv	474.4	-	2.720	1754.9	27.0	0.0	527.0	527.0
2	2150	Gas-purged line; with O_2; manifold; 15 min uv	458.0	-	2.660	1716.1	27.0	0.0	527.0	527.0
3	2123	Gas-purged line; with O_2; manifold; 30 min uv	469.1	-	2.700	1741.9	27.1	0.0	527.0	527.0
4	2150	Gas-purged line; with O_2; manifold; 30 min uv	494.1	-	2.880	1858.0	27.1	0.0	527.0	527.0
Method 7 510 cylinder (427.9 ppm)										
1	2058	Gas-purged line; manifold	433.3	414.3	2.410	1559.0	27.1	0.0	527.0	527.0
2	2072	Gas-purged line; manifold	419.9	414.3	2.350	1521.0	27.1	0.0	527.0	527.0
3	2105	Gas-purged line; manifold	430.6	414.3	2.450	1585.0	27.1	0.0	527.0	527.0

TABLE 7. LABORATORY TEST DATA SUMMARY (continued)

Test Method and Sample Number	Volume Flask	Remarks	NO_x, ppm	TECO, ppm	Absorbance	NO_2, mg	Pressure, in.Hg		Temperature, °R	
							Final	Initial	Final	Initial
Method 7 510 cylinder (427.9 ppm) (continued)										
4	2095	Unpurged gas line	352.2	414.3	2.100	1354.0	29.1	0.0	529.8	529.8
5	2058	Unpurged gas line	362.1	414.3	2.120	1367.0	29.1	0.0	529.8	529.8
6	2072	Unpurged gas line	371.3	414.3	2.190	1412.0	29.0	0.0	529.8	529.8
7	2086	Unpurged gas line	338.6	414.3	2.010	1296.0	29.0	0.0	529.8	529.8
Modified Method 7 510 cylinder (427.9 ppm)										
8	2104	Unpurged gas line	342.4	414.3	2.050	1322.0	29.1	0.0	529.8	529.8
9	2104	Unpurged gas line	375.8	414.3	2.250	1451.0	28.8	0.0	529.8	529.8
10	2104	Unpurged gas line	242.1	414.3	1.450	935.0	28.5	+0.2	529.8	529.8
11	2104	Unpurged gas line	400.1	414.3	2.350	1516.0	28.4	0.0	529.8	529.8
12	2104	Gas-purged line; with O_2	233.5	414.3	1.320	852.0	27.0	+0.1	529.8	529.8
13	2104	Gas-purged line; with O_2	263.4	414.3	1.480	961.0	27.1	+0.1	529.8	529.8

TABLE 7. LABORATORY TEST DATA SUMMARY (continued)

Test Method and Sample Number	Volume Flask	Remarks	NO_x, ppm	TECO, ppm	Absorbance	NO_2, mg	Pressure, in.Hg Final	Pressure, in.Hg Initial	Temperature, °R Final	Temperature, °R Initial
Modified Method 7 510 cylinder (427.9 ppm) (continued)										
14	2104	Gas-purged line; with O_2	285.0	414.3	1.580	1019.0	26.9	+0.1	529.8	529.8
15	2104	Gas-purged line; with O_2	222.0	414.3	1.230	794.0	26.8	+0.1	529.8	529.8
Method 7 500 cylinder (454.9 ppm)										
1	2072	Gas-purged line	450.5	455.3	2.500	1618.0	27.0	0.0	529.8	529.8
2	2095	Gas-purged line	442.1	455.3	2.480	1605.0	27.0	0.0	529.8	529.8
3	2105	Gas-purged line	431.2	455.3	2.430	1573.0	27.0	0.0	529.8	529.8
4	2086	Gas-purged line; manifold	451.5	455.3	2.550	1650.0	27.3	0.0	529.8	529.8
5	2058	Gas-purged line; manifold	463.3	455.3	2.580	1670.0	27.3	0.0	529.8	529.8
6	2090	Gas-purged line; manifold	456.1	455.3	2.580	1670.0	27.3	0.0	529.8	529.8
7	2086	Gas-purged line; manifold	452.1	455.3	2.540	1643.0	27.0	0.0	527.0	527.0

TABLE 7. LABORATORY TEST DATA SUMMARY (continued)

Test Method and Sample Number	Volume Flask	Remarks	NO_x, ppm	TECO, ppm	Absorbance	NO_2, mg	Pressure, in.Hg		Temperature, °R	
							Final	Initial	Final	Initial
Method 7 500 cylinder (454.9 ppm) (continued)										
8	2095	Gas-purged line; manifold	489.1	455.3	2.760	1785.0	27.0	0.0	527.0	527.0
9	2090	Gas-purged line; manifold	458.4	455.3	2.580	1669.0	27.0	0.0	527.0	527.0
Modified Method 7 500 cylinder (454.9)										
10	2104	Gas-purged line; with O_2; 15 min. uv	312.7	455.3	1.760	1140.0	27.0	0.0	529.8	529.8
11	2104	Gas-purged line; with O_2; 15 min. uv	408.4	455.3	2.300	1489.0	27.0	0.0	529.8	529.8
12	2104	Gas-purged line; with O_2; 15 min. uv	334.3	455.3	1.910	1237.0	27.4	0.0	529.8	529.8
13	2104	Gas-purged line; with O_2; 15 min. uv	373.8	455.3	2.120	1373.0	27.2	0.0	529.8	529.8
14	2104	Gas-purged line; with O_2; manifold; 15 min. uv	388.5	455.3	2.200	1424.0	27.0	0.0	527.0	527.0

TABLE 7. LABORATORY TEST DATA SUMMARY (continued)

Test Method and Sample Number	Volume Flask	Remarks	NO_x, ppm	TECO, ppm	Absorbance	NO_2, mg	Pressure, in.Hg Final	Pressure, in.Hg Initial	Temperature, °R Final	Temperature, °R Initial
Modified Method 7 500 cylinder (454.9) (continued)										
15	2157	Gas-purged line; with O_2; manifold; 15 min. uv	325.6	455.3	1.890	1224.0	27.0	0.0	527.0	527.0
16	2157	Gas-purged line; with O_2; manifold; 30 min. uv	421.9	455.3	2.420	1566.0	26.8	0.0	529.8	529.8
17	2104	Gas-purged line; with O_2; manifold; 30 min. uv	358.4	455.3	2.030	1314.0	27.0	0.0	527.0	527.0
18	2157	Gas-purged line; with O_2; manifold; 30 min. uv	416.6	455.3	2.200	1566.0	27.0	0.0	527.0	527.0
Method 7 60 cylinder (28.3 ppm)										
1	2105	Unpurged gas line	31.0	47.3	0.187	120.0	29.0	0.0	529.8	529.8
2	2090	Unpurged gas line	24.7	47.3	0.148	95.0	29.0	0.0	529.8	529.8
3	2113	Unpurged gas line	24.3	47.3	0.150	96.0	29.0	+0.4	529.8	529.8
4	2076	Unpurged gas line	30.2	47.3	0.176	113.0	28.6	-0.1	529.8	529.8

TABLE 7. LABORATORY TEST DATA SUMMARY (continued)

Test Method and Sample Number	Volume Flask	Remarks	NO_x, ppm	TECO, ppm	Absorbance	NO_2, mg	Pressure, in.Hg		Temperature, °R	
							Final	Initial	Final	Initial
Method 7 60 cylinder (28.3 ppm) (continued)										
5	2039	Unpurged gas line	32.6	47.3	0.190	122.0	28.8	0.0	529.8	529.8
6	2073	Unpurged gas line	27.0	47.3	0.161	103.0	29.1	0.0	529.8	529.8
7	2124	Gas-purged line	26.1	47.3	0.159	102.0	29.0	0.0	529.8	529.8
8	2120	Gas-purged line	20.1	47.3	0.125	80.0	29.1	+0.1	529.8	529.8
Modified Method 7 60 cylinder (28.3 ppm)										
9	2104	Gas-purged line	55.9	47.3	0.341	220.0	28.9	+0.3	529.8	529.8
10	2104	Gas-purged line	28.7	47.3	0.172	111.0	28.9	0.0	529.8	529.8
11	2104	Gas-purged line	25.4	47.3	0.155	100.0	29.0	+0.2	529.8	529.8
12	2104	Gas-purged line	32.0	47.3	0.195	126.0	29.3	+0.3	529.8	529.8
13	2104	Gas-purged line; with O_2	37.6	47.3	0.229	148.0	29.4	+2.7	529.8	529.8
14	2104	Gas-purged line; with O_2	34.0	47.3	0.207	134.0	29.3	+0.3	529.8	529.8

TABLE 7. LABORATORY TEST DATA SUMMARY (continued)

Test Method and Sample Number	Volume Flask	Remarks	NO_x, ppm	TECO, ppm	Absorbance	NO_2, mg	Pressure, in.Hg Final	Pressure, in.Hg Initial	Temperature, °R Final	Temperature, °R Initial
Modified Method 7 60 cylinder (28.3 ppm) (continued)										
15	2104	Gas-purged line; with O_2	29.0	47.3	0.164	106.0	27.0	+0.4	529.8	529.8
16	2104	Gas-purged line; with O_2	27.1	47.3	0.150	97.0	26.8	+0.2	529.8	529.8

[a]Data comparison:

Test Method (cylinder gas)	Sample Number	Avg., ppm	Standard Deviation	Samples in Calculation
MM7 (575 ppm)	1 & 2	466.2	8.2	2
	3 & 4	481.6	12.5	2
% difference MM7 1 & 2 versus MM7 3 & 4 = 3.2				
M7 (510 ppm)	1-3	427.9	5.36	3
	4-7	356.1	12.90	4
% difference M7 1-3 versus M7 4-7 = 16.8				
MM7 (510 ppm)	8,9,11	372.7	20.26	3
	12-15	250.9	23.20	4

Test Method (cylinder gas)	Sample Number	Avg. ppm	Standard Deviation	Samples in Calculation
M7 (500 ppm)	1- 9	454.9	10.48	9
MM7 (500 ppm)	10-15	351.2	33.01	6
	16-18	398.9	27.06	3
% difference MM7 10-15 versus MM7 16-18 = 10.4				
% difference MM7 10-15 versus M7 1-9 = 21.4				
% difference MM7 16-18 versus M7 1-9 = 12.3				
M7 (60 ppm)	1-6	28.3	2.90	6
	7-8	23.1	3.00	2

TABLE 7. LABORATORY TEST DATA SUMMARY (continued)

[a]Data comparison: (continued)

Test Method (cylinder gas)	Sample Number	Avg., ppm	Standard Deviation	Samples in Calculation
% difference MM7 8-11 versus MM7 12-15 = 32.7				
% difference MM7 12-15 versus M7 1-3 = 41.3				
% difference MM7 8-11 versus M7 1-3 = 12.9				

Test Method (cylinder gas)	Sample Number	Avg. ppm	Standard Deviation	Samples in Calculation
MM7 (60 ppm)	10-12	28.7	3.30	3
	13-16	31.9	3.80	4
% difference MM7 10-12 versus M7 7-8 = 19.5				
% difference MM7 13-16 versus M7 7-8 = 27.5				

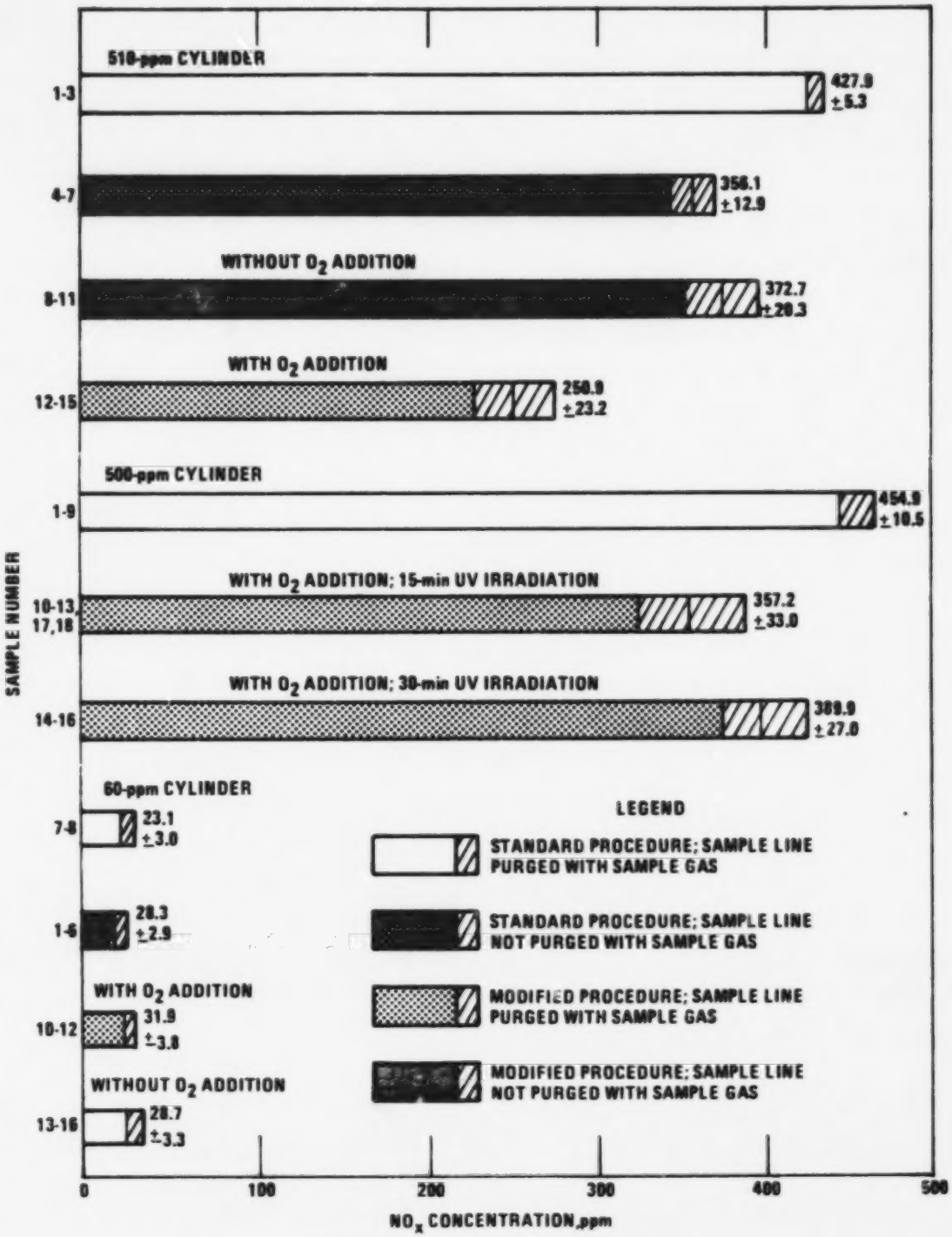

Figure 6. Laboratory data summary.

cylinder gas, delivered an instantaneous digital display of NO_x concentration in parts per million. Figure 7 illustrates the arrangement of the sampling apparatus at the SSSF.

The inlet rate of NO gas introduction was periodically varied, and as the gas recirculated through the source simulator, the total content of NO_x in the system increased. Because of the rather lengthy residence time of the NO inlet gas in the simulator (2 hours or more) and because of the presence of O_2 in the simulator, partial conversion of NO to NO_2 and N_xO_y occurred.

A plot of NO and NO_x values is shown in Figure 8. The plot contains data from both the TECO NO_x analyzer and the Philco-Ford Gas Filter Correlation instrument, which was undergoing preliminary testing at this site. The NO_x values for the Method 7 samples compare favorably (~98 percent correlation) with NO_x values measured by the TECO analyzer as well as with the GFC instrument (~40-60 percent correlation), which operated in the NO mode. The margin of difference between the TECO curve and the GFC curve represents the continuous oxidation of NO to NO_2 in the circulating system. The GFC curve indicates the amount of NO introduced in addition to the measurable content of NO retention in the simulation return loop.

Correlation among the three Method 7 data sets and the GFC NO and TECO NO_x data curves is depicted in as a chronological listing of experimental values in Table 8. A summary of Method 7 data may be found in Table 9.

The Simualted Source Testing Facility allowed the precise control and monitoring of NO concentrations as well as permitting the use of a wide range of NO_x sample concentrations. The utilization of these capabilities corroborated the assumption that the Method 7 procedure is reliable at a range of NO_x concentrations, that the repeatability between samples at static concentration is excellent (95 percent agreement), and that error caused by equipment failure and/or human error is minimal (<5 percent) under simulated field conditions.

Cape Fear Power Plant

The source used in the first field test of the modified method was the Cape Fear Station of the Carolina Power and Light Company, which is a 360-MW, coal-fired generating station. The testing was performed on the plant's Unit 9, which was an output of 120 MW. The duct that was used as the sampling site was 4 feet deep and approximately 2 feet wide; the sampling ports were spaced about 5 feet apart.

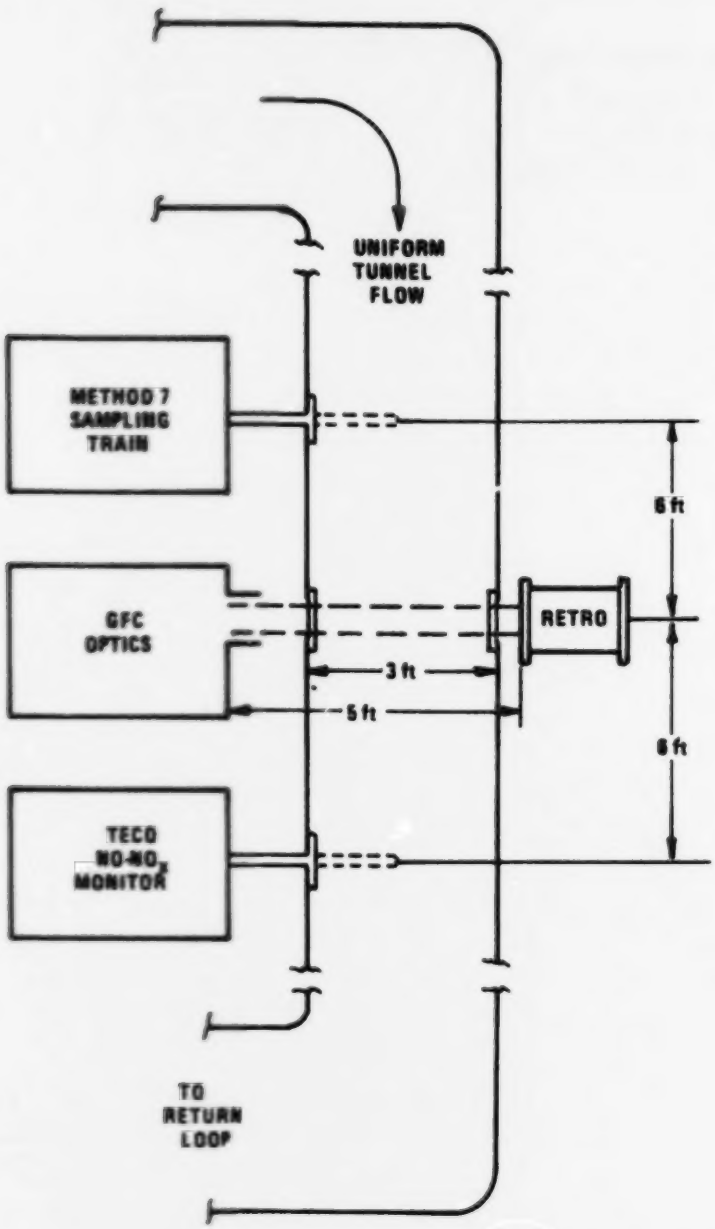

Figure 7. Stationary source simulator facility sampling arrangement.

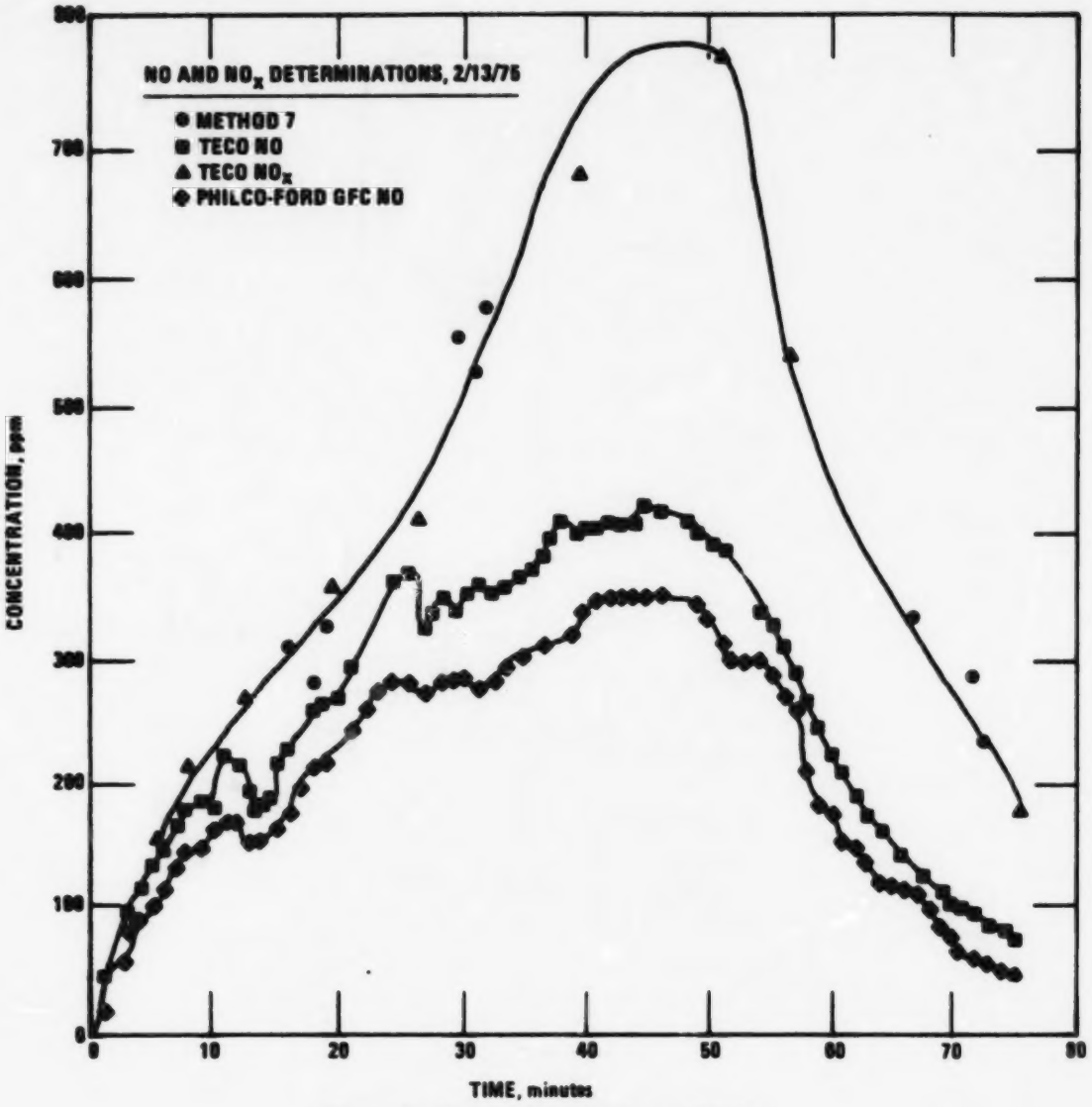

Figure 8. Method 7 evaluation at SSSF.

Table 8. CHRONOLOGICAL TECO, GFC, AND METHOD 7 DATA

Time, minutes	Method 7 ppm	NO added	GFC-NO, ppm	TECO NO_x, ppm
5.8	--	Yes	110	158
8.4	--	Yes	148	218
11.6	--	Yes	160	273
16.0	--	No	180	313
18.0	284	No	218	334
19.0	333	No	224	346
19.4	--	Yes	230	362
26.0	--	Yes	282	418
29.0	561	No	290	522
30.0	537	No	292	542
31.0	585	No	286	566
38.2	--	Yes	330	692
49.0	--	Yes	340	783
54.8	--	No	282	655
65.0	345	No	128	346
69.0	301	No	180	260
71.0	248	No	74	244
74.5	--	No	60	192

Time, minutes	Method 7 average NO_x, ppm	TECO NO_x, ppm	Percent agreement
16.0-19.0	310±10	331± 12	94
29.0-31.0	561±16	543± 45	97
65.0-71.0	298±34	283±145	95

TABLE 9. SUMMARY OF METHOD 7 NO_x DATA FROM STATIONARY SOURCE SIMULATOR FACILITY TEST, FEBRUARY 13, 1975[a]

Volume Flask (ml)	Sample Number	NO_x, ppm	TECO ppm	Absorbance	NO_2, mg	Pressure, in. Hg		Temperature, °R		Percent Agreement[b]
						Final	Initial	Final	Initial	
2039	1	313.9	323.0	1.840	1137	29.0	0.0	531.6	535.2	97.2
2076	2	284.9	345.1	1.690	1090	28.8	0.0	531.6	535.2	82.6
2120	3	333.1	356.5	2.030	1309	28.6	-0.4	531.6	535.2	93.5
2113	4	561.1	532.5	3.500	2258	28.8	-1.0	531.6	534.3	94.7
2124	5	537.0	549.5	3.440	2219	28.8	-1.6	531.6	534.3	97.8
2073	6	585.9	567.0	3.470	2238	28.3	-0.5	531.6	534.3	96.7
2090	7	345.9	417.5	2.230	1438	29.0	-2.1	531.6	532.5	82.9
2058	8	301.8	323.0	1.790	1155	28.8	-0.3	531.6	532.5	93.5
2086	9	248.1	275.0	1.490	961	28.9	-0.1	531.6	532.5	90.3

[a]Gas-purged line used in all tests; no O_2 was added. Barometric pressure was 29.63 for all tests.

[b]Based on agreement of TECO versus Method 7.

The rotary fan used to force-feed the stack was located downstream of the sampling site resulting in a negative sampling pressure of 10 inches of water. The plant layout and the sampling sites are shown in Figure 9.

Figure 2 shows the test equipment arrangement used at the sampling site. The probe was a 3/8-inch diameter stainless steel tube filled with glass wool to collect particulates. Teflon tubing was used for all connectors. The sampling flasks used were of two types: (1) the standard 2-liter sampling flask as shown in the Federal Register[3] and (2) a 2-liter, 2-neck, round bottom flask with no protective plastic foam outer coating (Figure 3). The latter type was used in the photochemical irradiation lamp studies. The flask pressures were monitored using a U-tube, mercury-filled manometer after evacuation had been accomplished with an oil-filled vacuum pump.

The test results of the field program at the Cape Fear plant are presented in Table 10.

Table 10. CAPE FEAR POWER PLANT TEST DATA

Series number	Sample number	Type	NO, ppm	
V	1	UV lamp	449	
	2	Method 7	569	(554)[a]
	3	Method 7	479	
	4	Method 7	587	
VI	1	UV lamp	409	
	2	Method 7	427	(470)[a]
	3	Method 7	513	
	4	Method 7	Sample lost	
VII	1	UV lamp	393	
	2	Method 7	401	(376)[a]
	3	Method 7	358	
	4	Method 7	370	
VIII	1	UV lamp	275	
	2	Method 7	480	(449)[a]
	3	Method 7	471	
	4	Method 7	396	

Mean for UV method: 429 ppm; standard deviation 85 ppm
Mean for Method 7: 466 ppm; standard deviation 85 ppm

[a] Value in parentheses is average using Method 7.

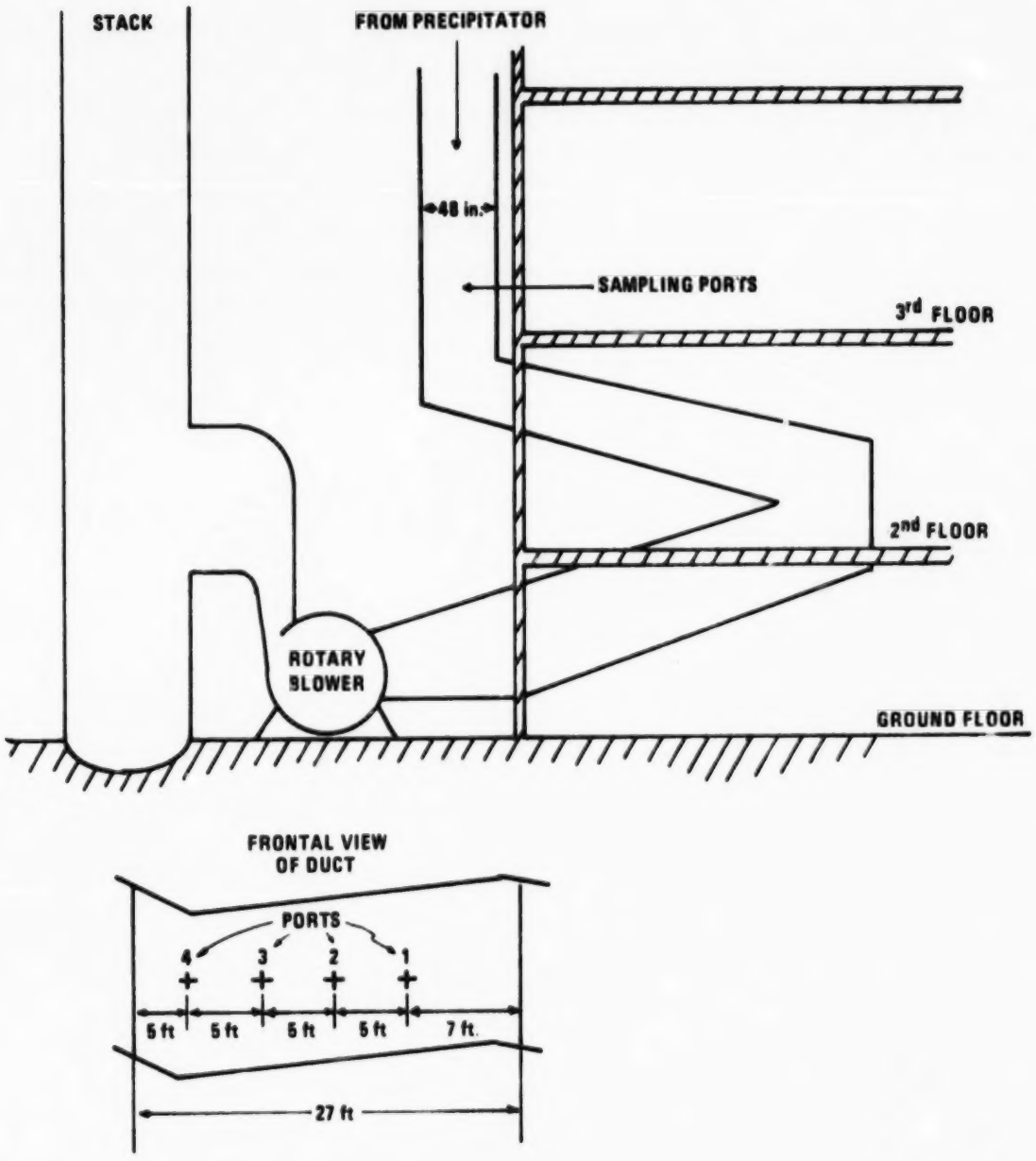

Figure 9. Sampling site configuration for CP&L Cape Fear Station Unit 9.

As can be seen from the data, the agreement between the Method 7 mean and the modified procedure values was relatively good (about 8 percent difference). The standard deviation of both the Method 7 and the modified Method 7 was rather poor (17-19 percent). This disagreement is probably caused by temporal and spatial stratification within the duct being sampled. Discussions with other EPA personnel who had worked at the site reinforced these assumptions. Velocity, temperature, and oxygen profiles of the duct showed spatial variations and temporal differences over a period of a week. Because of these difficulties, the comparative evaluation of the two methods was continued at the Duke Power Company station, which from previous experience appears to be a more suitable site.

River Bend Steam Generating Station

Duke Power Company's River Bend Station is a coal-fired steam generating station with an output capacity of 800 MW. During the test period, however, the plant was operated at approximately 75 percent of output capacity. Evaluation of Method 7 and modified Method 7 was performed on a boiler that produced a maximum output of 125 MW. The circular, vertical stack of the unit facilitated the horizontal placement of probes. Sampling ports were spaced concentrically about the 3-meter stack diameter. There were no internal obstructions for at least five stack diameters downstream, and except for microfluctuations resulting from subcapacity output, uniform flow characteristics were observed in the effluent.

The internal stack pressure was positive (about 3 inches of water) relative to atmospheric pressure and the internal stack temperature was about 135^{o}C.

Test equipment and sampling procedure used were identical with that of the Cape Fear Study.

Data obtained during experimentation are listed chronologically and summarized in Table II. An integrated chronological data plot is shown in Figure 10.

A DuPont NO_x analyzer was utilized to establish a continuously monitored data base for the work at River Bend. Unfortunately, because of unscheduled maintenance, the analyzer was inoperative during a majority of the experimentation. During the latter stages of work, however, the data generated from the DuPont are representative of the fluctuations in source NO_x level--if not also representative of the concentration of NO_x present. Both

TABLE 11. CHRONOLOGICAL SUMMARY OF DUKE POWER DATA

Sampling method and sample number	Average, ppm	DuPont condition[a] and correlation	Number of matrix samples
Method 7			
1-3	280.9 ± 2.2	Inoperative	3
4-6	260.8 ±14.7	Inoperative	3
13-15	307.6 ±10.5	Inoperative	3
18-20	318.0 ±12.2	Inoperative	3
23-25	284.4 ±22.1	Inoperative	2
28-30	318.9 ± 2.9	Inoperative	3
33-35	278.8 ± 9.3	86.8	3
38-40	234.8 ±20.0	97.9	3
43-45	204.5 ±45.2	83.1	3
46-48	259.7 ±12.8	77.1	3
Modified Method 7 (without O_2)			
7-10	260.4 ±16.8	Inoperative	3
51-52	284.3 ±34.9	82.6	2
53-54	223.7 ± 0.3	79.8	2
55-56	178.9 ±10.3	92.2	2
Modified Method 7 (with O_2)			
11-12	291.3 ± 1.0	Inoperative	2
16-17	288.2 ±61.3	Inoperative	2
21-22	273.2 ±42.0	Inoperative	2
26-27	290.2 ±79.9	Inoperative	2
31-32	212.0 ± 7.6	94.6	2
36-37	143.1 ±19.4	68.7	2
41-42	181.9 ±47.1	91.4	2
49-50	256.1 ±10.0	81.2	2

[a]DuPont inoperative; no comparison possible.

Method 7 and DuPont samples drawn simultaneously indicate observable source fluctuation with approximately 90 percent correlation. The DuPont analyzer has a response time lag of about 10 minutes because of the need to pressurize the NO_x sample with O_2 for conversion of NO-NO_2. The time lag should be noted during critical evaluation of the graphic representation of accumulated data (Figure 10).

Modified Method 7 samples 7-10 and 51-56, which were taken with no O_2 addition, show no effect under the conditions encountered at the River Bend Station. The rate of the reaction $2NO+O_2$-$2NO_2$ is dependent on $[NO]^2$ and $[O_2]$. In the case of the River Bend Station $[O_2]$= 6 percent, a rather large excess with respect to the 150-250 ppm NO typically was encountered. Because excess O_2 already exists in the stack sample, the introduction of additional O_2 would not be expected to have an appreciable effect. In future work, an evaluation of plant operating conditions should be made in order to anticipate the need for O_2 addition.

Figure 10 illustrates the correlation between Method 7 and modified Mehtod 7. The agreement ranges from 55 percent in samples 36 and 37 to 95 percent in samples 43-45. Overall correlation was computed by averaging all deviations of modified Method 7 from the reference method data plot.

A complete data summary from River Bend Steam Station is found in Table 12.

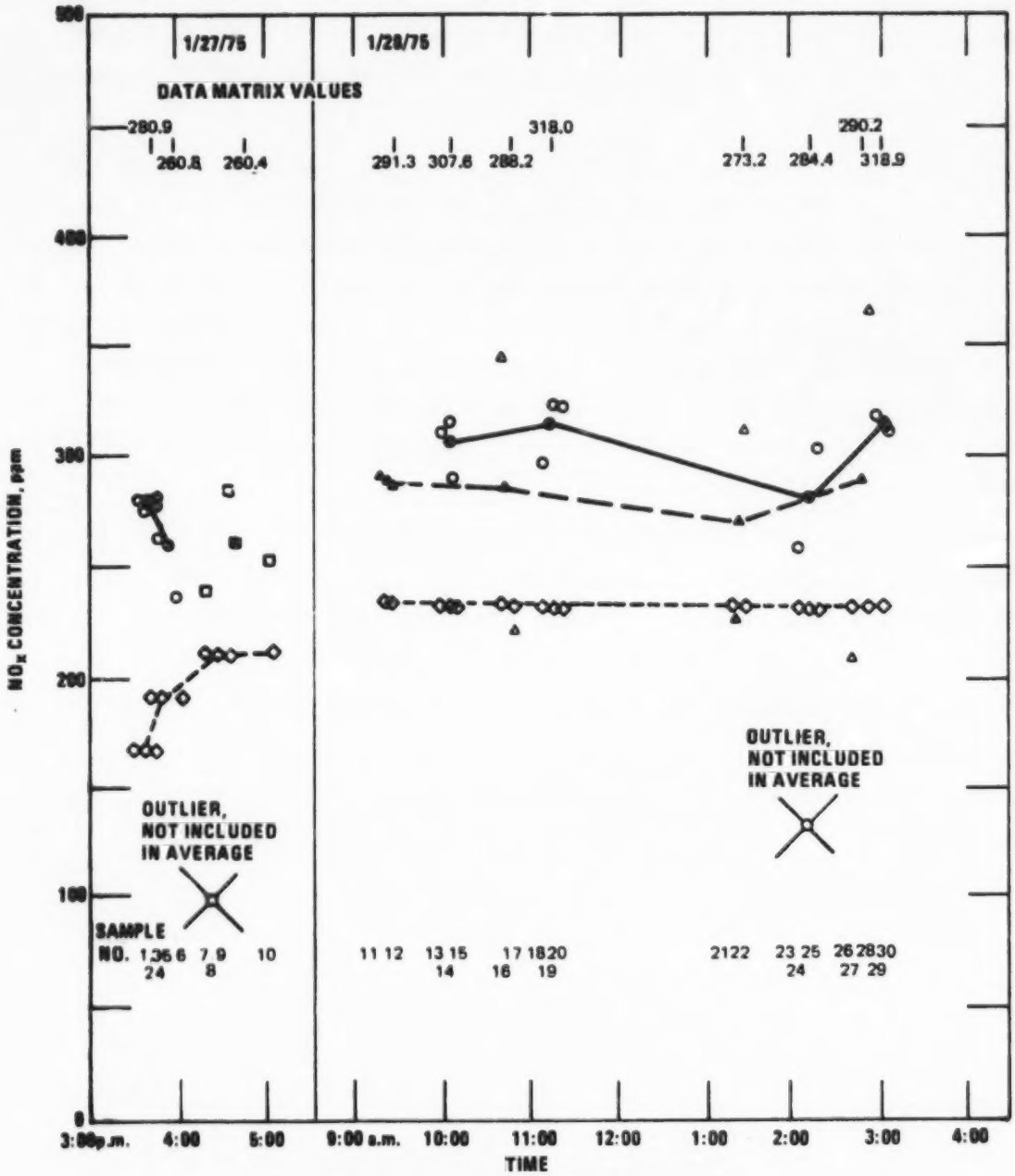

Figure 10. Integrated M7, MM7, and duPont data.

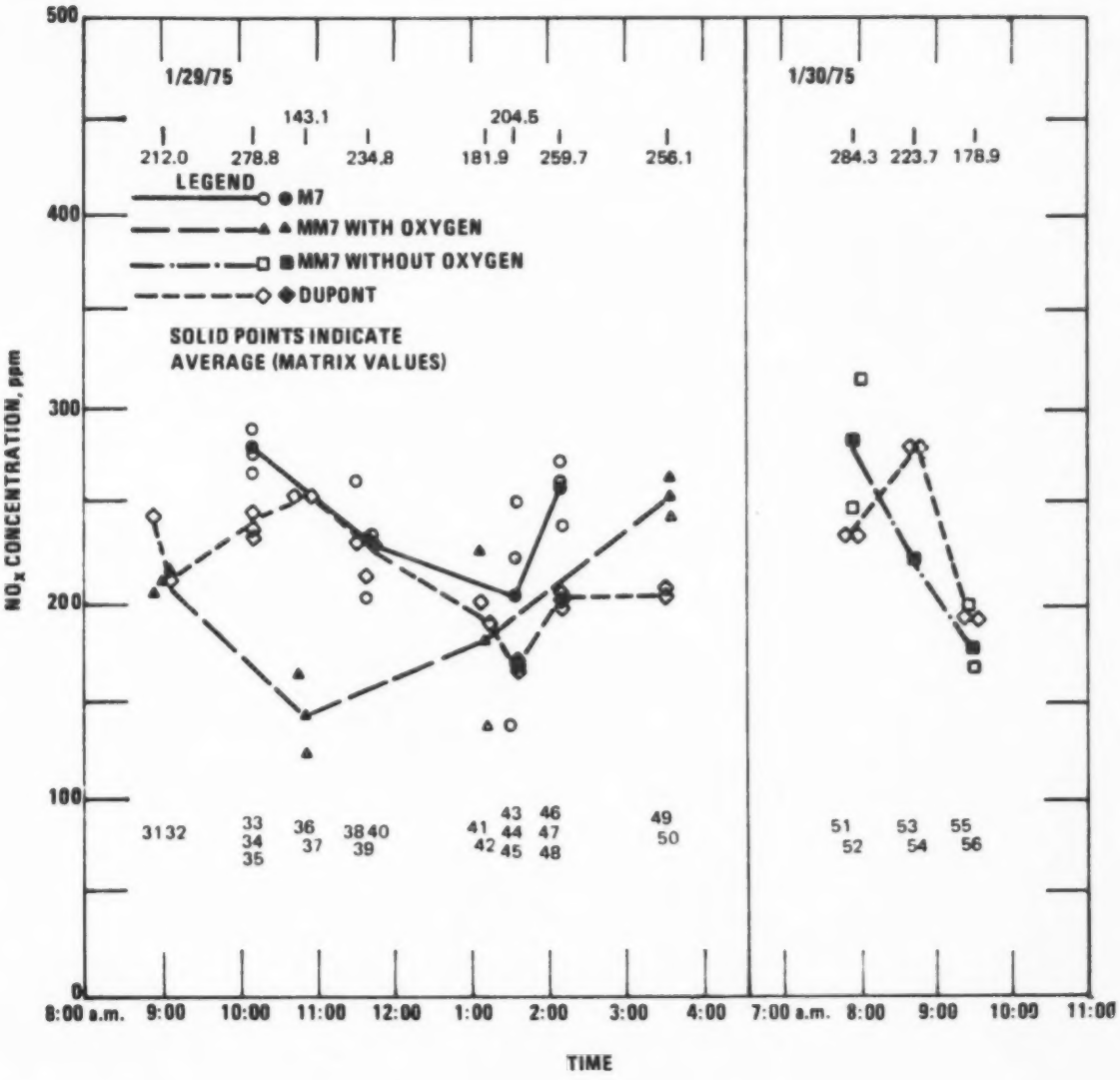

Figure 10 (continued). Integrated M7, MM7, and duPont data.

TABLE 12. SUMMARY[a] OF FIELD TEST DATA FROM DUKE POWER COMPANY RIVERBEND STATION

Sampling Conditions and Sample number[b]	Volume Flask	NO_x, ppm	DuPont ppm	Absorbance	NO_2, mg	Pressure, in. Hg		Temperature, °R		Time and Day	Barometric Pressure
						Final	Initial	Final	Initial		
Method 7 tests Sampling line purged											
1	2120	282.9	168.0[c]	1.740	1122	28.8	-0.6	534.3	542.4	3:30 27	29.52
2	2095	277.6	168.0[c]	1.720	1110	28.6	-1.4	534.3	542.4	3:35 27	29.52
3	2105	282.2	168.0[c]	1.730	1115	28.6	-0.9	534.3	542.4	3:40 27	29.52
4	2124	280.6	190.4[c]	1.730	1115	28.8	-0.6	534.3	542.4	3:40 27	29.52
5	2073	263.1	190.4[c]	1.580	1020	28.7	-0.7	534.3	542.4	3:45 27	29.52
6	2090	238.7	190.4[c]	1.440	930	28.4	-0.9	534.3	542.4	3:55 27	29.52
13	2039	312.9	235.2[c]	1.810	1167	29.0	+0.3	533.4	529.8	9:50 28	29.58
14	2076	318.0	235.2[c]	1.880	1212	29.0	+0.2	533.4	529.8	10:00 28	29.58
15	2072	291.9	235.2[c]	1.710	1103	28.9	+0.1	537.0	529.8	10:05 28	29.58
18	2113	299.7	235.2[c]	1.790	1155	28.8	0.0	537.0	535.2	11:05 28	29.58
19	2058	327.7	235.2[c]	1.900	1225	28.9	+0.4	533.4	534.3	11:10 28	29.58
20	2086	326.7	235.2[c]	1.900	1225	28.8	+0.6	533.4	534.3	11:15 28	29.58
23	2095	262.3	235.2[c]	1.540	995	28.1	-0.5	537.0	540.6	2:00 28	29.55
24	2120	134.3[d]	235.2[c]	0.810	523	28.6	-0.4	537.0	540.6	2:05 28	29.55
25	2105	306.5	235.2[c]	1.850	1193	28.6	-0.6	537.0	540.6	2:10 28	29.55
28	2073	323.4	235.2[c]	1.800	1245	28.4	-0.5	537.0	541.5	2:50 28	29.53
29	2090	318.2	235.2[c]	1.730	1217	28.7	-0.2	537.0	541.5	2:55 28	29.53
30	2124	315.2	235.2[c]	1.720	1217	28.5	-0.2	537.0	541.5	3:00 28	29.53

TABLE 12. SUMMARY[a] OF FIELD TEST DATA FROM DUKE POWER COMPANY RIVERBEND STATION (continued)

Sampling Conditions and Sample number[b]	Volume Flask	NO_x, ppm	DuPont ppm	Absorbance	NO_2, mg	Pressure, in. Hg		Temperature, °R		Time and Day	Barometric Pressure
						Final	Initial	Final	Initial		
Method 7 tests Sampling line purged (continued)											
33	2086	292.9	235.2	1.580	1103	28.7	0.0	540.6	539.7	10:10 29	29.45
34	2095	269.1	246.4	1.420	1000	28.1	-0.1	540.6	539.7	10:10 29	29.45
35	2058	274.6	235.2	1.440	1013	28.5	0.0	540.6	540.6	10:10 29	29.45
38	2090	263.5	235.2	1.430	1008	28.4	-0.7	540.6	540.6	11:30 29	29.43
39	2120	204.8	212.8	1.090	781	28.3	-0.3	540.6	540.6	11:35 29	29.43
40	2113	236.1	235.2	1.290	910	28.6	-0.4	540.6	540.6	11:40 29	29.43
43	2073	136.7	168.0	1.280	904	27.9	-2.3	540.6	545.1	1:30 29	29.33
44	2105	223.5	168.0	1.300	917	28.7	-2.3	540.6	545.1	1:30 29	29.33
45	2124	253.3	168.0	1.390	981	28.0	-1.0	540.0	545.1	1:30 29	29.33
46	2072	275.3	201.6	1.460	1026	28.2	-0.4	540.6	545.1	2:05 29	29.31
47	2039	240.5	201.6	1.270	897	28.1	-1.0	540.6	545.1	2:05 29	29.31
48	2076	263.4	201.6	1.390	980	28.4	-0.1	540.6	545.1	2:05 29	29.31
Modified Method 7 tests Sampling line purged; without O_2											
7	2157	241.5	212.8[c]	1.430	923	28.6	+0.3	543.3	543.3	4:15 27	29.52
8	2104	99.3[d]	212.8[c]	0.540	370	28.6	+0.3	543.3	543.3	4:20 27	29.52
9	2157	285.7	212.8[c]	1.690	1090	28.6	+0.4	542.4	542.4	4:30 27	29.52

TABLE 12. SUMMARY[a] OF FIELD TEST DATA FROM DUKE POWER COMPANY RIVERBEND STATION (continued)

Sampling Conditions and Sample number[b]	Volume Flask	NO_x, ppm	DuPont ppm	Absorbance	NO_2, mg	Pressure, in. Hg Final	Pressure, in. Hg Initial	Temperature, °R Final	Temperature, °R Initial	Time and Day	Barometric Pressure
Modified Method 7 tests Sampling line purged; without O_2 (continued)											
10	2104	254.1	212.8[c]	1.460	942	28.4	+0.3	542.4	542.4	5:00 27	29.52
51	2157	249.4	235.2	1.380	975	28.3	-0.5	540.6	540.6	7:50 30	29.49
52	2104	319.2	235.2	1.840	1187	28.3	+0.2	540.6	540.6	7:55 30	29.48
53	2104	224.0	280.0	1.200	852	28.8	+0.2	537.9	539.7	8:40 30	29.52
54	2157	223.5	280.0	1.290	911	28.4	-0.2	537.9	539.7	8:45 30	29.53
55	2157	189.2	190.4	1.030	743	28.5	-0.2	536.1	538.8	9:25 30	29.55
56	2104	168.7	190.4	0.880	646	28.4	-0.3	536.1	539.7	9:30 30	29.56
Sampling line purged; with O_2											
11	2104	292.3	235.2[c]	1.760	1135	29.0	+0.1	532.5	532.8	9:15 28	29.58
12	2157	290.3	235.2[c]	1.780	1150	29.0	+0.2	533.4	529.8	9:20 28	29.58
16	2104	349.5	235.2[c]	2.090	1348	28.9	+0.1	534.3	531.6	10:35 28	29.58
17	2157	227.0	235.2[c]	1.400	905	28.8	-0.2	534.3	531.6	10:45 28	29.58
21	2104	231.2	235.2[c]	1.350	872	28.5	0.0	540.6	538.8	1:15 28	29.56
22	2157	315.2	235.2[c]	1.910	1232	28.7	-0.1	540.6	538.8	1:20 28	29.56
26	2157	210.3	235.2[c]	1.130	808	28.3	-0.1	542.4	541.5	2:35 28	29.54
27	2104	370.2	235.2[c]	2.150	1387	28.4	0.0	542.4	541.5	2:45 28	29.54

TABLE 12. SUMMARY[a] OF FIELD TEST DATA FROM DUKE POWER COMPANY RIVERBEND STATION (continued)

Sampling Conditions and Sample numberb	Volume Flask	NO_x, ppm	DuPont ppm	Absorbance	NO_2, mg	Pressure, in. Hg Final	Pressure, in. Hg Initial	Temperature, °R Final	Temperature, °R Initial	Time and Day	Barometric Pressure
Sampling line purged; with O_2 (continued)											
31	2104	204.4	246.4	1.070	767	28.6	+0.2	541.5	534.3	8:55 29	29.46
32	2157	219.6	212.8	1.190	845	28.6	+0.2	541.5	535.2	9:05 29	29.46
36	2157	162.5	257.6	0.850	633	28.5	-0.2	540.6	540.6	10:45 29	29.45
37	2104	123.8	257.6	0.620	472	28.6	-0.2	540.6	540.6	10:50 29	29.45
41	2104	229.0	201.6	1.200	852	28.4	+0.1	544.2	543.3	1:05 29	29.36
42	2157	134.9	190.4	0.680	511	28.2	+0.1	544.2	543.3	1:10 29	29.36
49	2104	266.1	207.2	1.390	980	28.0	-0.1	546.0	545.1	3:30 29	29.28
50	2157	246.1	207.2	1.330	936	28.2	-0.1	546.0	545.1	3:30 29	29.28

[a]Data comparison:

Method 7 (line purged)				Modified Method 7 (line purged)				
Sample number	Average, ppm	Standard deviation, ppm	Number of samples in calculation	Remarks	Sample number	Average, ppm	Standard deviation, ppm	Number of samples in calculation
1,2,3	280.9	2.20	3	without	7-10	260.4	16.83	3
4,5,6	260.8	14.73	3	O_2 added	51-52	284.3	34.90	2

TABLE 12. SUMMARY[a] OF FIELD TEST DATA FROM DUKE POWER COMPANY RIVERBEND STATION (continued)

[a]Data comparison: (continued)

Method 7 (line purged)				Modified Method 7 (line purged)				
Sample number	Average, ppm	Standard deviation, ppm	Number of samples in calculation	Remarks	Sample number	Average, ppm	Standard deviation, ppm	Number of samples in calculation
13-15	307.6	10.46	3		53-54	223.7	0.30	2
18-20	318.0	12.23	3		55-56	178.9	10.30	2
23-25	284.4	22.10	2		11-12	291.3	1.00	2
28-30	318.9	2.96	3		16-17	288.2	61.30	2
33-35	278.8	9.33	3		21-22	273.2	42.00	2
38-40	234.8	20.00	3		26-27	290.2	79.90	2
43-45	204.5	45.20	3		31-32	212.0	7.60	2
46-48	259.7	12.83	3		36-37	143.1	19.40	2
					41-42	181.9	47.10	2
					49-50	256.1	10.00	2

[b]Samples numbered sequentially as taken.

[c]DuPont in repair.

[d]Equipment failure.

SECTION VI
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